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⑰ Applicant: ICI AMERICAS INC  
Concord Pike & New Murphy Road  
Wilmington Delaware 19897(US)

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⑱ Inventor: Gills, Herbert  
4706 Apple Lane  
West Deptford New Jersey 08066(US)

⑲ Designated Contracting States:  
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⑳ Representative: Leherte, Georges Maurice  
Lucien Marie et al  
Imperial Chemical Industries PLC Legal  
Department: Patents P.O. Box 6  
Welwyn Garden City Herts. AL7 1HD(GB)

㉑ Liquid organic polyisocyanate compositions containing urea and/or biuret structures.

㉒ Modified organic isocyanate composition containing urea and/or biuret groups, and/or salts of these groups, prepared by reacting a blocked amine composition and a polyisocyanate composition, said blocked amine composition being the reaction product of:

a. a primary and/or secondary organic amine composition having an average amine functionality of at least 0.1 and an average total active hydrogen functionality of from about 1.5 to about 10.0, and  
b. a reactivity modifying agent selected from proton acids, Lewis acids, silylating agents, metalating agents and alkylating agents, and said polyisocyanate composition comprising organic polyisocyanates and/or polyisothiocyanates having a reactive isocyanate and/or isothiocyanate functionality of at least 1.0, the reaction between said blocked amine and polyisocyanate compositions being conducted so as to provide an excess of isocyanate and/or isothiocyanate groups over total active hydrogens in the blocked amine composition of at least 1.5 : 1.0.

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This invention relates to liquid organic polyisocyanate compositions containing urea and/or biuret structures and to methods for preparing said composition.

Because of the advantageous effects which can be provided by the introduction of urea and/or biuret into polyurethanes, it is well known to modify organic polyisocyanates by the incorporation therein of urea and/or biuret groups and then to use the modified isocyanates in polyurethane manufacture.

Urea group modified isocyanates may be obtained by reacting organic polyisocyanates with a stoichiometric deficiency of water or a mono- or polyamine. Under the influence of heat, the ureas can then react with further polyisocyanates to form biurets. In many cases, however, the biuret-modified polyisocyanates, which are usually homogeneous solutions, are difficult to produce because the initially formed ureas are insoluble solids which react further only with difficulty.

In order to overcome this problem, it has been proposed in U.S. Patent No. 3441588 to react the polyisocyanates with a polyether diamine and it is said that biuret prepolymers are conveniently prepared without the undesirable formation of solid urea precipitates.

It has now surprisingly been found that isocyanate compositions which contain significant quantities of urea and/or biuret terminated structures may be prepared quite conveniently by rapid mixing of certain blocked or "retarded" polyamines with polyisocyanates. The reactions may be performed at low temperature (i.e. ambient, or slightly above). When appropriate blocking or retarding agents are used, the functionalities of the reagents (amine and/or isocyanate) may be higher than 2. The use of high-functionality reagents, either individually or in combination, does not necessitate any increase in the severity of the reaction condition (i.e. the temperature of reaction). This represents a very significant improvement, in processing convenience, over prior art methods. Modified isocyanate compositions which have previously been inaccessible or impractical may now be prepared with surprising ease. Most of the modified isocyanate (even the highest functionality combinations) exhibit surprising homogeneity and stability at ambient temperatures. The compositions are generally clear, free of solids, and low in viscosity.

Accordingly, the invention provides a modified organic isocyanate composition containing urea and/or biuret groups, and/or salts of these groups, prepared by reacting a blocked amine composition and a polyisocyanate composition, said blocked amine composition being the reaction product of :

5 a. a primary and/or secondary organic amine composition having an average amine functionality of at least 0.1 and an average total active hydrogen functionality of from about 1.5 to about 10.0, and

10 b. a reactivity modifying agent selected from proton acids, Lewis acids, silylating agents, metallating agents and alkylating agents, and said polyisocyanate composition comprising organic polyisocyanates and/or polyisothiocyanates having a reactive isocyanate and/or isothiocyanate functionality of at least 1.0, the reaction between said blocked amine and polyisocyanate compositions being conducted so as to provide an excess of isocyanate and/or isothiocyanate groups over total active hydrogens in the blocked amine composition of at least 1.5 : 1.0.

15 Organic amine compositions suitable for use in preparing the isocyanate compositions of the invention are preferably those having a primary and/or secondary amine functionality of at least 1. Particularly preferred composition include primary and/or secondary amine containing polyamines having number averaged amine functionalities of between about 2 and about 6 and having amine equivalent weights above about 100, the term "number averaged amine functionality being used to refer to the average number of primary and secondary amine groups  $n$  in an average polyamine molecule. In addition to the primary and/or secondary amino groups, the organic amine composition may contain other types of active hydrogen containing groups, for example hydroxy, carboxy and thiol groups, such that the total active hydrogen functionality is up to about 10.0.

20 25 30 35 40 45 Especially preferred organic amine compositions include primary and/or secondary amino terminated polyethers such as have been described in US Patent No. 3441588. Suitable amino terminated polyethers include polyether amines and polyether polyamines having average amine functionalities of from about 0.1 to about 3.0 and preferably from 0.5 to 2.1. Particular mention may be made of amino terminated polyethers based on ethylene oxide, propylene oxide, tetrahydrofuran and mixtures thereof, especially those having molecular weights in the range of 500 to 8000.

50 55 Examples of commercial amine terminated polyethers which are preferred for use in the instant invention include Jeffamine D-4000, a 4000 molecular weight primary amine terminated polypropylene oxide diamine; Jeffamine D-2000, a 2000 molecular weight primary amine terminated polypropylene oxide diamine; Jeffamine T-5000, a 5000 molecular weight primary amine terminated polypropylene oxide triamine; Jeffamine T-3000, a 3000 molecular weight primary amine terminated polypropylene oxide triamine; Jeffamine ED-2001, a 2000 molecular weight primary amine terminated

polyoxypropylene polyoxyethylene copolymer diamine; and Jeffamine ED-600, a 600 molecular weight primary amine terminated polyoxypropylene polyoxyethylene copolymer diamine; or mixtures thereof.

Suitable blocking or retarding, or "reactivity modifying" agents, for use with the aforementioned amines, include any anhydrous proton acid. Particularly suitable proton acids include hydrohalic acids such as hydrofluoric, hydrochloric, hydrobromic, or hydroiodic acids; lower molecular weight carboxylic acids such as acetic acid, propionic acid, benzoic acid, adipic acid, terephthalic acid, trifluoroacetic acid, trichloroacetic acid, carbonic acid, hydroxyacetic acid, acrylic acid, methacrylic acid, oxalic acid, malonic acid, fumaric acid, succinic acid, mixtures thereof, and the like; sulfonic acids such as methanesulfonic acid, benzenesulfonic acid, toluenesulfonic acid, trifluoromethane sulfonic acid, polystyrene sulfonic acid(s), and mixtures thereof; phosphonic acids such as phenylphosphonic acid, methylphosphonic acid, butylphosphonic acid, and the like. In some instances it may be acceptable to use the mineral oxyacids such as sulfuric acid, boric acid, nitric acid, nitrous acid, sulfurous acid, phosphoric acid, arsenic acid, silicic acid, and the like materials; provided that these are substantially free of water and can be made compatible with the amine composition. In some instances it may be possible to employ blocking or retarding agents which are essentially aprotic but which will form labile complexes with the amine. These species include  $CS_2$ ,  $CO_2$ ,  $SO_2$ ,  $SO_3$ , etc.; and Lewis acids such as inorganic or organic salts of magnesium, calcium, aluminium, iron, manganese, cobalt, zinc, lithium, boron, etc. Some specific examples of the Lewis acidic materials include zinc propionate, calcium sulfate and hydrates thereof, magnesium acetate and hydrates thereof, magnesium chloride and its hydrates, triphenylboron, hydrated alumina, ferric chloride, and the like. Finally, it is in many instances possible to use blocking or retarding agents which are essentially permanent in nature, in the sense that their action results in the conversion of primary amines into slower reaction. These permanent blocking agents will remain associated with the nitrogen atoms of the amine even after these nitrogen atoms have been reacted with isocyanates to form the urea and/or biuret modified compositions of the invention. Such permanent blocking agents include silylating agents such as trimethylsilylchloride, triethylsilyl bromide, trimethylsilylnitrile, trimethylsilylazide, t-butyl-dimethylsilyl chloride, trimethylsilyl imidazole, trimethylsilane, and like materials; various organic alkylating agents such as t-butyl chloride, acrylonitrile, acrylamide, methyl methacrylate,

dimethyl fumarate, butyl acrylate, isopropyl cinamate, diphenylmethyl chloride, triphenylmethyl chloride, 1-chloroethylbenzene, 1-bromopropylbenzene, neopentyl bromide, and like materials or mixtures of such materials. It may, in some instances, be acceptable to use organometallic blocking agents such as trimethylgermanyl chloride, tributylstannyli chloride, triethyl borate, tri-n-butyl silicate, dicyclopentadienyltitanium dichloride, dicyclopentadienylniobium trichloride, mercuric acetate, and similar materials.

The choice of a blocking agent will depend upon a large number of factors, such as cost, availability, solubility in the amine, the degree of difficulty involved in preparing the blocked amine, storage stability of the blocked amine, etc. In all cases, however, it is critical that the blocking or retarding agent be chosen so as to reduce the reactivity of the amine towards isocyanates, without actually preventing this reaction. The blocked amines must eventually react to form urea and/or biuret structures, in the presence of organic isocyanates. Accordingly, blocking agents or conditions which result in the formation of tertiary amine or quaternary ammonium species must be avoided because these types of amine derivatives cannot form urea and/or biuret species, in the presence of isocyanates. When alkylating or metallating agents are used, the agent itself and the reaction conditions must be chosen in such a way as to limit polyalkylation or polymetallation of the amine nitrogen atoms. It is, therefore, preferred that the number of reactive equivalents of alkylating or metallating agents used should be less than or equal to the number of equivalents of reactive primary amines present in the substrate amine(s). It is preferred, further, that the alkylating or metallating agents be chosen so as to provide, subsequent to reaction with the amine, a degree of steric hinderance in order to inhibit a second alkylation or metallation at the same position(s). Alkylating or metallating agents which provide steric bulk at the site of reaction are greatly preferred over those which do not. Bulky agents such as trimethylsilylnitrile are preferred over smaller alkylating agents such as methyl iodide. When labile blocking agents are used, such as the acids described hereinabove, it is preferred that the number of reactive equivalents of blocking agents used be less than or equal to the number of reactive equivalents of primary and secondary amines present in the amine substrate composition. If an excess of the labile blocking agent is used, relative to the quantity of amine groups present, then it is preferred that some provision should be made for removal or neutralization of the excess blocking agent subsequent to the blocking reaction.

When choosing blocking agents, whether permanent or labile, the compatibility of the blocking agent and/or the blocked amine and/or the ultimate decomposition products of the blocking agent with the isocyanate substrate composition must be allowed for. In particular, it is greatly preferred that the storage stability and the ultimate reactivity of the urea and/or biuret modified isocyanate compositions of the invention not be compromised by impurities introduced from the blocking operation. It is further preferred that these impurities not result in the prolonged evolution of toxic or obnoxious by-products from the urea and/or biuret modified isocyanate compositions. The choice of blocking agent is therefore partly dependent upon the properties or characteristics of the final urea and/or biuret modified compositions, and of polymeric compositions derived therefrom.

According to a preferred embodiment of the invention, the blocking agent and the amine composition are combined and mixed in appropriate amounts, along with any appropriate catalysts, in a chemical reactor and heated to a temperature and pressure which are sufficient to promote the desired blocking reaction. The resulting mixture is agitated until the reaction has reached the desired degree of completion. According to the most preferred embodiments, the "chemical reactor" is simply a static (in-line) mixer or an impingement mixing apparatus into which the reagent streams are fed at a rate, temperature, pressure, and weight ratio which is most appropriate for the desired blocking reaction. Under this, most preferred, processing arrangement, the need for bulky processing equipment and for lengthy synthetic operations is largely eliminated. If necessary or desired, however, for example when compatibility between the blocking agent and the amine composition is poor, the reaction may be performed in the presence of a solvent.

Polyisocyanate compositions which may be used in preparing the isocyanate compositions of the invention include the aliphatic and aromatic polyisocyanates already known in the polyurethane art.

Suitable aliphatic polyisocyanates include ethylene, hexamethylene and dicyclohexylmethane diisocyanates. Suitable aromatic polyisocyanates include toluene and diphenylmethane diisocyanates. The preferred polyisocyanate is 4,4'-diphenylmethane diisocyanate which may be used as the pure compound or in a liquid modified form, for example a prepolymer or uretonimine-modified MDI. Other useful polyisocyanates include mixtures of 4,4'-MDI with the 2,4' and 2,2'-isomers as well as crude products containing MDI together with higher functionality polymethylene polyphenyl polyisocyanates.

Examples of commercial polyisocyanates include Rubinate-44; Rubinate LF-168; Rubinate XI-208; experimental diisocyanate composition 4397-49 (approximately an 80:20 mole/mole blend of 4,4'-diphenylmethane diisocyanate with 2,4'-diphenylmethane diisocyanate, which also contains minor amounts of 2,2'-diphenylmethane diisocyanate); or mixtures of the above; all from Rubicon Chemicals Inc. Of course the term polyisocyanate also includes quasi-prepolymers of polyisocyanates with polyols. Examples of such materials are Rubinate LF-179 and Rubinate LF-167 (prepolymer modified MDI products); also available from Rubicon Chemicals Inc.

The urea and/or biuret modified isocyanate composition of the invention may be prepared by reacting the blocked amine composition and the polyisocyanate composition in the presence or absence of solvents. Suitable solvents include benzene, toluene, chlorobenzene, o-dichlorobenzene, butyl acetate, ethylene glycol monomethyl ether acetate, methyl ethyl ketone, chloroform, methylene chloride, and the like.

Preferably, the reaction is performed in the absence of solvents in a static (in-line) mixer or an impingement mixing apparatus into which the reagent streams are fed at a rate, temperature, pressure and weight ratio appropriate for preparing the desired compositions.

The reaction temperature may be as high as 200 deg. C at pressures of up to 1000 atmospheres although it is not generally necessary to exceed temperatures of 100 deg. C or pressures of 100 atmospheres. The preferred temperature range is between 20 and 50 deg. C at pressures of from 1 to 10 atmospheres. Generally, the higher reaction temperature and the longer the residence time at a given temperature, the greater the extent of biuret formation. A low level of functionality and hence a low level of biuretisation is generally desirable when the isocyanate compositions are intended for use in the manufacture of elastomeric or flexible materials. For the production of for example rigid foam, a higher level of biuretisation may be desirable making it appropriate to use more severe conditions for the reaction between the blocked amine composition and the polyisocyanate composition.

The urea and/or biuret modified isocyanate compositions of the invention may be prepared by using an excess of isocyanate groups (i.e., including any isothiocyanate groups) over active hydrogen groups of at least 1.5:1 on an equivalent basis. In the more preferred embodiments of the invention, however, the ratio of isocyanate groups to the sum total of active hydrogen groups used to prepare the modified isocyanate compositions of the invention is at least 3:1, on an equivalents basis. In

the most preferred embodiments, the ratio of isocyanate groups to the sum total of active hydrogen groups used to prepare the modified isocyanate compositions of the invention is at least 5:1, on an equivalent basis. The "active hydrogen groups" referred to hereinabove are to be understood as the sum of the reactive (primary and secondary) amine groups present (whether free, or in "blocked" or latent form) within the blocked polyamine composition, and any additional Zerewitinoff active hydrogen groups, such as alcohols, phenols, thiols, carboxylic acids, and the like.

The modified isocyanate compositions of the invention may be used in the manufacture of polyurethane, polyurethaneurea, polyurea and polyamide materials by reaction with appropriate active hydrogen compounds under appropriate conditions. Suitable active hydrogen compounds include organic compounds containing a plurality of amino, hydroxy, carboxy or thiol groups. Such compounds generally have molecular weights of from 200 to 10,000, preferably between 500 and about 5000.

Amino-containing compounds which may be reacted with the isocyanate compositions include those already described herein, for example amino-terminated polyether.

Hydroxy compounds which may be reacted with the isocyanate compositions include the polyether and polyester polyols already known for use in the manufacture of polyurethanes. Polyesteramides and polyacetals may also be employed. The polyethers particularly include the oxyalkylation products of active hydrogen compounds, for example products obtained by reacting ethylene oxide and/or propylene oxide with polyols or polyamines. Suitable polyesters include the reaction products of glycols and other polyols with aliphatic and/or aromatic dicarboxylic acids.

The reaction between modified isocyanate compositions and the active hydrogen compounds may be performed under conditions that have been fully described in the polyurethane literature. Thus, the reaction may be performed in the presence, as appropriate, of blowing agents, for example water and/or trichlorofluoromethane, catalysts, for example tertiary amines and/or tin compounds, surfactants, for example siloxane-oxyalkylene copolymers, chain-extenders, for example glycols or diamines, pigments, fillers, flame-retardants and the like.

The products obtained by reacting the isocyanate compositions with active hydrogen compounds may take the form of flexible or rigid foams, solid elastomers, coatings and the like. Where appropriate it is preferred to use the reac-

tion injection moulding (RIM) process. The invention is illustrated but not limited by the following Examples.

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#### Glossary of Terms :

Polyamine A : A linear 2000 molecular weight primary amine terminated polyoxypropylene diamine, which is commercially available from Texaco Chemical Corp. "Jeffamine D-2000".

Polyamine B : A linear 400 molecular weight primary amine terminated polyoxypropylene diamine, which is commercially available from Texaco Chemical Corp. as "Jeffamine D-400".

Polyamine C : A linear 4000 molecular weight primary amine terminated polyoxypropylene diamine, which is commercially available from Texaco Chemical Corp. as "Jeffamine D-4000".

Polyamine D : A glycerol initiated 5000 molecular weight primary amine terminated polyoxypropylene triamine, which is commercially available from Texaco Chemical Corp. as "Jeffamine T-5000".

Polyamine E : A glycerol initiated 3000 molecular weight primary amine terminated polyoxypropylene triamine, which is commercially available from Texaco Chemical Corp. as Jeffamine T-3000.

Polyamine F : A linear 2000 molecular weight polyoxyethylene polyoxypropylene copolymer based diprimary diamine in which about 94 mole percent of the total oxyalkylene units in the chain are oxyethylene units and the remaining 8 mole percent are oxypropylene units. This substance is commercially available from Texaco Chemical Co. as "Jeffamine ED-2001".

Polyamine G : A linear 600 molecular weight primary amine terminated polyoxyethylene polyoxypropylene copolymer diamine in which about 77 mole percent of the total oxyalkylene units in the chain are oxyethylene units and the remaining 23 mole percent are oxypropylene units. This substance is commercially available from Texaco Chemical Co. as "Jeffamine ED-600".

Polyamine H : An 80:20 mixture, by weight, of 3,5-diethyl-2,4-diaminotoluene and 3,5-diethyl-2,6-diaminotoluene. A commercially available mixture of aromatic diprimary diamines, as obtained from Ethyl Corporation.

Isocyanate I : Pure 4,4'-diphenylmethane diisocyanate, containing not more than 2 % by weight of the 2,4'-diphenylmethane diisocyanate isomer. This material is commercially available from Rubicon Chemicals Inc.

Isocyanate J : A mixture consisting of approximately 80 % by weight of 4,4'-diphenylmethane diisocyanate and about 20 % by weight 2,4'-diphenylmethane diisocyanate. Commercially available from Rubicon Chemicals Inc.

Isocyanate K : A uretonimine modified derivative of Isocyanate I, having a free isocyanate - (NCO) content of 29.3 % by weight and a number averaged functionality of about 2.15. This substance is commercially available from Rubicon Chemicals Inc., as "Rubinate LF-168".

Isocyanate L : A uretonimine modified derivative of Isocyanate J, having a free isocyanate - (NCO) content of 31.0 % by weight and a number averaged functionality of about 2.08. This substance is commercially available from Rubicon Chemicals Inc., as "Rubinate XI-208".

Isocyanate M : Phenyl isocyanate.

Isocyanate N : A urethane pseudoprepolymer modified derivative of Isocyanate I which is prepared by reacting Isocyanate I with a mixture of low molecular weight glycols. This substance has a free isocyanate (NCO) content of about 23.0 % by weight, a number averaged functionality of 2.00, and is commercially available from Rubicon Chemicals Inc., as "Rubinate LF-179".

Isocyanate O : A blend consisting of 50% by weight Isocyanate K and 50% by weight Isocyanate N. This substance is commercially available from Rubicon Chemicals Inc. as "Rubinate LF-167".

Isocyanate P : A mixture consisting of about 70% by weight of 4,4'-diphenylmethane diisocyanate and about 30 % 2,4'-diphenylmethane diisocyanate.

Isocyanate Q : A mixture consisting of about 80% 2,4-toluene diisocyanate and about 20% 2,6-toluene diisocyanate. This substance is commercially available from Rubicon Chemicals Inc. as "Rubinate TDI".

Isocyanate R : Is the meta isomer of tetramethylxylylene diisocyanate. This material is commercially available from American Cyanamide Corp. as "m-TMXDI".

Isocyanate S : Polymeric polyphenylmethane polyisocyanate, or "crude MDI". A mixture of various isomers of diphenylmethane diisocyanate with a series of higher functionality methylene bridged polyphenylmethane isocyanates, in a ratio of about 1:1 by weight. This substance has a number averaged isocyanate functionality of about 2.75 and a functional group (NCO) concentration of about 31.5% by weight. It is commercially available from Rubicon Chemicals Inc. as "Rubinate M".

Isocyanate T : A modified version of Isocyanate S, in which the diphenylmethane diisocyanate isomer content has been increased, by blending with Isocyanate J. This substance has

5 a number averaged isocyanate functionality of about 2.40 and a functional group (NCO) concentration of about 31.5% by weight. It is commercially available from Rubicon Chemicals Inc. as "Rubinate XI-182".

10 Examples 1-10 are intended to illustrate convenient methods for preparing the blocked, "retarded", or "reactivity modified" polyamine compositions which are useful in the practice of the instant invention.

### Example 1

15 A flask was charged with 350 g of Polyamine D. The flask, equipped with a thermometer, overhead stirrer, and an inert gas inlet, was gently and continuously purged with a stream of dry nitrogen. A gas sparging tube was inserted into the flask, with the outlet well below the level of liquid (Polyamine D). The liquid was gently agitated and sparged, beneath its surface, with anhydrous hydrochloric acid (HCl) in large excess. The excess HCl was swept out of the flask via the nitrogen purge. The HCl sparging was initiated at ambient temperatures (20-25 Deg C.) and continued until after the reaction exotherm had peaked and subsided. The total reaction time was 1 hr. (HCl sparging) and the peak exotherm reached 53 Deg.C. 20 during this preparation. The product was a clear liquid.

### Example 2

25 35 Following the procedure analogous to that described in Example 1, a 350 g sample of the anhydrous hydrochloride salt of Polyamine E was prepared. The total sparging time was approximately 1 hr. The product was a clear liquid.

### Example 3

40 45 Following the procedure analogous to that described in Example 1, a 350 g sample of the anhydrous hydrochloride salt of Polyamine G was prepared. The total sparging time was approximately 1 hr. The product was a clear liquid.

## Example 4

Following the procedure analogous to that described in Example 1, a 350 g sample of the anhydrous hydrochloride salt of Polyamine C was prepared. The total sparging time was approximately 1 hr. The product was a clear liquid.

## Example 5

A flask, equipped with thermometer, overhead stirrer, and a purge of dry nitrogen, was charged with 300 g of Polyamine C. Adipic acid, 11.0 g, was then suspended in the liquid polyamine. The resulting suspension was agitated and heated until all the solids dissolved. The system became clear and homogeneous at 85 deg C. The product remained homogeneous at ambient temperatures.

## Example 6

Following a procedure analogous to that described in Example 5, a 300 g sample of Polyamine D was modified with 13.16 g of adipic acid. The adipic acid was initially suspended in the polyamine. The system was then heated until clear (85 deg. C). The product was a clear homogeneous liquid at ambient temperatures.

## Example 7

A flask was charged with 325 g of Polyamine C. The flask, equipped with a thermometer, overhead stirrer, and an inert gas inlet, was gently and continuously purged with a stream of dry nitrogen. A gas purging tube was inserted into the flask, with the outlet well below the level of liquid (Polyamine C). The liquid was gently agitated and sparged, beneath its surface, with anhydrous carbon dioxide (CO<sub>2</sub>) in large excess. The excess CO<sub>2</sub> was swept out of the flask via the nitrogen purge. The CO<sub>2</sub> sparging was initiated at 23 Deg C. and continued until after the reaction exotherm had peaked and subsided. The total reaction time was 1 hr. (CO<sub>2</sub> sparging) and the peak exotherm reached 30 Deg.C during this preparation. The product was a clear liquid.

## Example 8

Following a procedure analogous to that described in Example 7, a 325 g sample of the carbon dioxide modified derivative of Polyamine A was prepared. The total sparging time was approximately 1 hr and the peak exotherm reached 34 deg.C. The product was a clear liquid.

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## Example 9

A flask was charged with 283.2 g of Polyamine D. The flask, equipped with a thermometer, an overhead stirrer, and an inert gas inlet, was maintained under a slight positive pressure with dry nitrogen. The liquid Polyamine D was agitated and trimethylsilylnitrile, 18.85 g., was added steadily via syringe over a period of 2 min. The temperature of the reaction increased from 23 deg. C to 31 deg. C during the addition -due to a spontaneous exotherm. Modest gas evolution was noted. This gas was allowed to expand against the nitrogen back pressure and escape through a side outlet in the nitrogen line. The gas was vented into a fume hood. After the addition was completed, the temperature of the reaction was increased to 80 deg. C over 13 min. and maintained at 80 deg. C, with continued agitation, for an additional 40 min. The flask was then attached to a vacuum line and the pressure over the liquid mixture was reduced from ambient to approximately 1 mm.Hg. Vigorous gas evolution was noted during this depressurization step. This gas was condensed in a dry ice trap. The outlet from the vacuum pump was vented into a fume hood. Gas evolution was observed to have ceased 8 min. after the vacuum was applied. The temperature of the system was further increased to 105 deg. C over a period 10 min. Heating was then discontinued and the product was allowed to cool. Agitation was discontinued and the pressure in the flask was allowed to increase, to ambient, by introduction of dry nitrogen. The product was a clear liquid.

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## Example 10

Following a procedure closely analogous to that used in Example 9, a sample consisting of 100 g of Polyamine B was reacted with 49 g of trimethylsilylnitrile. The total reaction time was 83 min., the maximum temperature reached during the vacuum degassing stage was 100 deg. C, and the final product was a clear liquid.

## Example 11

A sample of the polyamine derivative prepared in Example 2 was added directly to a 90:10 (w/w) blend of Isocyanate J and K. The addition was performed at a temperature of 46 deg. C under an atmosphere of dry nitrogen. The isocyanate blend was agitated gently throughout the addition. The addition was conducted over a period of 43 min. Following the addition, the pressure within the reaction vessel was reduced to approximately 1 mm. Hg. and agitation was continued for 1 hr. longer. Pressure within the vessel was then increased to ambient, by slow introduction of dry nitrogen. Agitation was discontinued and the sample was stored, under an atmosphere of dry nitrogen, at ambient temperatures. The product was observed to be a clear homogeneous liquid. The product was free of solids, gels, or cloudiness after 3 weeks of storage. No solids or gels were observed at any point during the preparation. The final formulation is listed below, with each ingredient as a percent by weight of the total :

Isocyanate J = 45.0 %

Isocyanate K = 5.0 %

Derivative of Polyamine E (from Example 2) = 50.0 %

Attempts to form a composition analogous to that shown under Example 11, according to a procedure analogous to that described in Example 11, but using untreated Polyamine E (instead of the derivative prepared in Example 2) were not successful. Solids began forming instantly when Polyamine E was added to the isocyanate blend of Example 11. Continued addition of Polyamine E resulted in a steady buildup of gel-like solids.

## Example 12

A sample of the polyamine derivative prepared in Example 1 was added directly to a 90:10 (w/w) blend of Isocyanate J and K. The addition was performed at a temperature of 48 deg. C under an atmosphere of dry nitrogen. The isocyanate blend was agitated gently throughout the addition. The addition was conducted over a period of 26 min. Following the addition, the pressure within the reaction vessel was reduced to approximately 1 mm. Hg. and agitation was continued for 1 hr. longer. Pressure within the vessel was then increased to ambient, by slow introduction of dry nitrogen. Agitation was discontinued and the sample was stored, under an atmosphere of dry nitrogen, at ambient temperatures. The product was observed to be a

clear homogeneous liquid. The product was free of solids, gels, or cloudiness after 6 weeks of storage. No solids or gels were observed at any point during the preparation. The final formulation is listed below, with each ingredient as a percent by weight of the total :

Isocyanate J = 45.0 %

Isocyanate K = 5.0 %

Derivative of Polyamine D (from Example 1) = 50.0 %

Attempts to form a composition analogous to that shown under Example 12, according to a procedure analogous to that described in Example 12, but using untreated Polyamine D (instead of the derivative prepared in Example 1) were not successful. Solids began forming instantly when Polyamine D was added to the isocyanate blend of Example 12. Continued addition of Polyamine D resulted in a steady buildup of gel-like solids.

## Example 13

A sample of the polyamine derivative prepared in Example 3 was added directly to a sample of Isocyanate L. The procedure followed was closely analogous to that used in Examples 11 and 12, except that the addition time was 15 min. and the vacuum treatment of the crude product was omitted. The maximum temperature reached during the processing 50 deg. C. A sample of the product was transferred to a dry glass jar and allowed to cool, at ambient temperature, for 1 hr. under an atmosphere of dry nitrogen. The product was a clear liquid which was free of solids or gels. The final formulation is listed below, with each ingredient as a percent by weight of the total :

Isocyanate L = 95.0 %

Derivative of Polyamine G (from Example 3) = 5.0 %

Attempts to form a composition analogous to that shown under Example 13, according to a procedure analogous to that described in Example 13, but using untreated Polyamine G (instead of the derivative prepared in Example 3) were not successful. Solids began forming rapidly when Polyamine G was added to Isocyanate L. Continued addition resulted in a steady buildup of gel-like solids. These solids would not re-dissolve, even when the temperature of the heterogeneous mixture was increased to 80 deg. C.

## Example 14

A sample of the polyamine derivative of Example 2 was added directly to a sample of Isocyanate S.

The isocyanate was agitated gently during the addition and the reaction vessel was purged continuously with dry nitrogen. The addition was conducted over less than 2 min. at an initial temperature of 22 deg. C. The temperature of the system increased to 42 deg. C., due to the exotherm of the reaction. No solids or gels were observed during or after the addition, but the viscosity of the formulation increased to the point where further agitation became labored. The formulation is listed below, with each ingredient as percent by weight :

Isocyanate S = 50.0 %

Derivative of Polyamine E (from Example 2) = 50.0 %

In order to reduce the viscosity of the modified isocyanate composition to manageable levels, the above formulation was back blended with Isocyanate S and the temperature of the initial blend was increased momentarily to 55 deg. C. in order to facilitate the mixing. The final formulation is listed below with each ingredient as a percent by weight.

Isocyanate S = 75.0 %

Derivative of Polyamine E (from Example 2) = 25.0 %

This final product was transferred to a dry glass jar and stored at ambient temperatures under an atmosphere of dry nitrogen. The product was observed to be a clear homogenous liquid, free of solids or gels, after 7 days of storage. No solids, gels, or other signs of inhomogeneity were observed at any point during the preparation or storage of this product.

Attempts to form a composition analogous to that shown under Example 14, according to a procedure analogous to that described in Example 14, but using untreated Polyamine E (instead of the derivative prepared in Example 2), were not successful. Solids began forming when the first drop of Polyamine E was added to Isocyanate S. Continued addition of Polyamine E resulted in a steady buildup of gel-like solids.

## Example 15

A sample of the polyamine derivative of Example 10 was added directly to a sample of Isocyanate L.

The isocyanate was agitated during the addition and the reaction vessel was purged continuously with a stream of dry nitrogen. The addition was conducted over 0.5 hrs. at a temperature of 50 deg. C. The formulation thus prepared is listed below, with each ingredient as percent by weight :

Isocyanate L = 75.0 %

Derivative of Polyamine B (from Example 10) = 25.0 %

This product, although homogeneous in bulk, was highly viscous at ambient temperatures. A sample of the product was reheated to 47 deg. C. and back blended with Isocyanate L, with gentle agitation, to give the final formulation listed below :

Isocyanate L = 85.0 %

Derivative of Polyamine B (from Example 10) = 15.0 %

This final product was transferred to a dry glass jar and stored at ambient temperatures under an atmosphere of dry nitrogen. The product was observed to be a clear pourable liquid and remained homogenous in bulk after 1 month of storage.

Attempts to form a composition analogous to that shown under Example 15, according to a procedure analogous to that described in Example 15, but using untreated Polyamine B (instead of the derivative prepared in Example 10), were not successful. Solids began forming when the first drop of Polyamine B was introduced to Isocyanate L. Continued addition of Polyamine B resulted in a steady buildup of gel-like solids. These solids would not redissolve when the temperature of the reaction was increased to 80 deg. Celsius.

## Example 16

A sample of the polyamine derivative prepared in Example 9 was added directly to a blend of Isocyanate J and K. The isocyanate blend was agitated continuously during the addition and the reaction vessel was purged with a stream of dry nitrogen. The addition was conducted over a period of 26 min. at a temperature of 50 deg. C. The formulation thus prepared is listed below, with each ingredient as percent by weight :

Isocyanate J = 45.0 %

Isocyanate K = 5.0 %

Derivative of Polyamine D (from Example 9) = 50.0 %

This product was clear, liquid and free of solids or gels at the conclusion of this reaction.

Example 17

A sample of the polyamine derivative prepared in Example 8 was rapidly poured into a well agitated sample of Isocyanate L. This addition took place over a period of not more than 5 sec. The reaction vessel, containing the isocyanate, was continuously purged with dry nitrogen during the addition and subsequent mixing. The addition was conducted with both components at ambient temperatures. The formulation thus prepared is listed below, with each ingredient as percent by weight :

Isocyanate L = 75.0 %

Derivative of Polyamine A (from Example 8) = 25.0 %

Within about 5 sec. of the addition, vigorous foaming was observed. The system foamed to more than twice its original volume. This foaming rapidly subsided, and there remained a homogeneous liquid product. The reaction was accompanied by a mild exotherm. The maximum temperature reached during this experiment was 33 deg. C. The product was allowed to cool, with gentle agitation, for 10 min. and was then transferred to a dry glass jar and sealed under an atmosphere of dry nitrogen. After approximately 12 hrs. storage at ambient temperatures, the product was found to have a viscosity of 975 cps (at 23 deg. C.). The product was a clear homogeneous liquid, free of solids or gels. No solids, gels, or separations were observed at any point during the preparation of this product.

Attempts to form a composition analogous to that shown under Example 17, according to the procedure of Example 17, but using untreated Polyamine A (instead of the derivative prepared in Example 8), were not successful. Soft gelatinous semi-solids began forming during the addition of Polyamine A to Isocyanate L. At the conclusion of

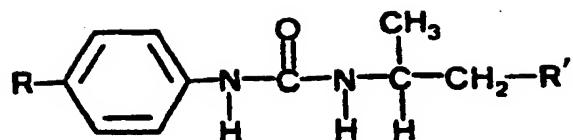
the reaction the product was clearly heterogeneous, with gelled solids evident. After approximately 12 hrs. storage at ambient temperatures, the product was found to have a viscosity of 3685 cps (at 23 deg. C.). The product was opaque, heterogeneous, and showed evidence of bulk separation.

Example 18

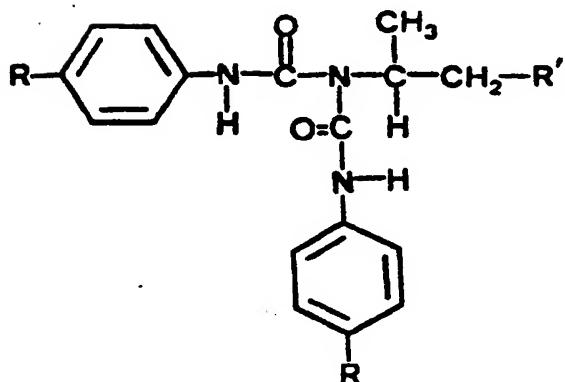
A bis-urea model compound was prepared by reacting Polyamine A with Isocyanate M, so as to provide 0.99 equivalents of isocyanate (NCO) per equivalent of amine (NH<sub>2</sub>). The amine was, therefore, used in slight excess. The reaction was performed by mixing the ingredients, at ambient temperatures, under an atmosphere of dry nitrogen. The product of this reaction was a clear colourless liquid which exhibited a carbonyl stretch in the infrared spectrum at 1698 cm<sup>-1</sup>.

A model biuret compound was prepared by reacting Polyamine A with Isocyanate M so as to provide 2.02 equivalents of isocyanate groups per equivalent of NH<sub>2</sub> or, in other words, 1.01 equivalents of "NCO" per equivalent of amine hydrogen. Thus a slight excess of isocyanate was used in the preparation. The reaction was performed by initially mixing the ingredients at ambient temperature, followed by heating at 120 deg. C. for 75 min. and then 85 deg. C. for 30 min.. Under an atmosphere of dry nitrogen. The product was a clear pale yellow liquid which exhibited a principal carbonyl stretch in the infrared spectrum at 1721 cm<sup>-1</sup>. This peak was notably absent in the spectrum of the model urea compound described hereinabove. Moreover, the starting polyamine and isocyanate used to prepare the model compounds are devoid of carbonyl species and, hence, devoid of carbonyl absorptions in the infrared (the NCO group is, strictly speaking, an exception to this rule; but its absorption occurs above 2200 cm<sup>-1</sup> which places it well above the region of interest).

This particular pair of model compounds was selected because they contain key structural elements which are identical to those present in many of the modified isocyanate compositions which are compared in past examples. The structural elements are :

urea

and

biuret

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wherein R represents hydrogen or a-CH<sub>2</sub>-terminated organic radical and R' represents a polyether chain. It is therefore possible to locate signals in the spectra of the modified polyisocyanate compositions which are homologous to those of the model compounds. In this way, the progress of the biuretization reaction can be followed as a function of processing conditions. The spectroscopic results can be compared to the concentration of residual isocyanate (NCO) groups in the sample. It is possible, also, to assess whether or not the blocked, or reactivity modified, polyamine composition has indeed reacted with the isocyanate substrate composition to form urea and/or biuret linkages. The presence of carbonyl signals in the IR (below 2200 cm<sup>-1</sup>) is generally diagnostic of reaction. Infrared analyses were performed on the modified isocyanate compositions prepared in Examples 11, 12, 14, 15, 17 and 18. These analyses showed the presence of the new carbonyl species, formed in the reaction between the isocyanate and blocked polyamine.

## Claims

- 35 1. A modified organic isocyanate composition containing urea and/or biuret groups, and/or salts of these groups, prepared by reacting a blocked amine composition and a polyisocyanate composition, said blocked amine composition being the reaction product of:
  - 40 a. a primary and/or secondary organic amine composition having an average amine functionality of at least 0.1 and an average total active hydrogen functionality of from about 1.5 to about 10.0, and
  - 45 b. a reactivity modifying agent selected from proton acids, Lewis acids, silylating agents, metallating agents and alkylating agents, and said polyisocyanate composition comprising organic polyisocyanates and/or polyisothiocyanates having a reactive isocyanate and/or isothiocyanate functionality of at least 1.0, the reaction between said blocked amine and polyisocyanate compositions being conducted so as to provide an excess of isocyanate and/or isothiocyanate groups over total active hydrogens in the blocked amine composition of at least 1.5 : 1.0.
- 50 2. A modified isocyanate composition according to claim 1 wherein the organic amine composition has a primary and/or secondary amine functionality of at least 1.

3. A modified isocyanate composition according to claim 2 wherein the organic amine composition has an average amine functionality of between about 2 and about 6 and an amine equivalent weight above about 100.

4. A modified isocyanate composition according to claims 1 to 3 wherein the organic amine composition is an amino terminated polyether having an average amine functionality of from about 0.1 to about 3.0.

5. A modified isocyanate composition according to claim 4 wherein the amino terminated polyether has an average functionality of from 0.5 to 2.1.

6. A modified isocyanate composition according to claim 4 or claim 5 wherein the amino terminated polyether has a molecular weight in the range of 500 to 8000 and is based on ethylene oxide, propylene oxide, tetrahydrofuran or mixtures thereof.

7. A modified isocyanate composition according to claims 1 to 6 wherein the polyisocyanate composition is or includes a diphenylmethane diisocyanate.

8. A modified isocyanate composition according to claims 7 wherein the polyisocyanate composition is or includes a 4,4'-diphenylmethane diisocyanate.

9. A modified isocyanate composition according to claim 8 wherein the polyisocyanate composition comprises a mixture of 4,4'-diphenylmethane diisocyanate with the 2,4'-and 2,2'-isomers.

10. A modified isocyanate composition according to claims 1 to 9 wherein the ratio of isocyanate and/or isothiocyanate groups to total active hydrogens in the blocked amine composition is at least 3:1.

11. A modified isocyanate composition according to claim 10 wherein the ratio of isocyanate and/or isothiocyanate group to total active hydrogens in the blocked amine composition is at least 5:1.

12. A polyurethane, polyurethaneurea, polyurea or polyamide material obtained by reacting a modified organic isocyanate composition according to claims 1 to 11 with a compound containing a plurality of active hydrogens atoms.

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⑰ Applicant: ICI AMERICAS INC  
Concord Pike & New Murphy Road  
Wilmington Delaware 19897(US)

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⑰ Inventor: Gillis, Herbert  
4706 Apple Lane  
West Deptford New Jersey 08066(US)

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Lucien Marie et al  
Imperial Chemical Industries PLC Legal  
Department: Patents P.O. Box 6  
Welwyn Garden City Herts. AL7 1HD(GB)

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⑯ Liquid organic polyisocyanate compositions containing urea and/or biuret structures.

⑯ Modified organic isocyanate composition containing urea and/or biuret groups, and/or salts of these groups, prepared by reacting a blocked amine composition and a polyisocyanate composition, said blocked amine composition being the reaction product of:

a. a primary and/or secondary organic amine composition having an average amine functionality of at least 0.1 and an average total active hydrogen functionality of from about 1.5 to about 10.0, and

b. a reactivity modifying agent selected from proton acids, Lewis acids, silylating agents, metal-lating agents and alkylating agents, and said polyisocyanate composition comprising organic polyisocyanates and/or polyisothiocyanates having a reactive isocyanate and/or isothiocyanate functionality of at least 1.0, the reaction between said blocked amine and polyisocyanate compositions being conducted so as to provide an excess of isocyanate and/or isothiocyanate groups over total active hydrogens in the blocked amine composition of at least 1.5 : 1.0.

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EP 86 30 5934

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)		
A	EP-A-0 012 970 (BAYER) * Page 9, line 1 - page 12, line 25; page 16, line 22 - page 17, line 9; claims 1,2 *	1	C 08 G 18/10 C 08 G 18/32 C 08 G 18/76		
A	US-A-3 976 622 (WAGNER et al.) * Column 6, lines 30-42; column 10, line 13 - column 11, line 4; claim 1 *	1			
A	US-A-4 136 241 (AMMANN) * Column 2, lines 12-42; claim 1 *	1			
A	EP-A-0 135 867 (BAYER) * Page 2, line 20 - page 3, line 22; page 8, line 11 - page 16, line 26; claim 1 *	1-9	TECHNICAL FIELDS SEARCHED (Int. Cl.4)		
D, A	US-A-3 441 588 (WAGNER et al.) * Claims 1-18 *	1-12	C 08 G		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	29-05-1987	BOURGONJE A.F.			
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